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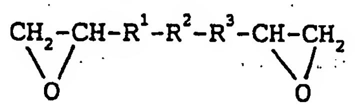
(54) Resin composition for sealing film-made liquid crystal cells.

(57) A resin composition for sealing liquid crystal cells comprising as principal ingredients epoxy resin containing a polysulfide modified epoxy resin, hydrazide compounds and fillers.

Said epoxy resin may contain a polysulfide modified epoxy resin expressed by the general formula (1) by 20 to 100% by weight in the entire epoxy resin and the average molecular weight of the entire epoxy resin is preferably between 300 and 3000.



(1)

where each of R^1 and R^3 represents at least one organic group selected from a group consisting of bisphenol structures, aliphatic oxyether structures and aliphatic thioether structures and R^2 represents a polysulfide structure expressed by $-(C_2H_4OCH_2OC_2H_4S_m)_n-$, wherein m represents the number of sulfur atoms contained in a polysulfide structure, which is 1 or 2, and n represents the average number of polysulfide structures contained in the above formula, which is between 1 and 50.

A film-made liquid crystal cell made by using the resin composition is excellent in adhesion, flexibility, electric properties and has high reliability.

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This invention relates to a novel resin composition to be suitably used for sealing liquid crystal displays of a variety of types developed in recent years and to be reliably operated in severe environments. It also relates to a film-made liquid crystal cell realized by using such a resin composition.

In recent years, liquid crystal displays have become markedly popular in response to the rapid development of down-sized personal computers, audio equipment, instruments, color television sets and other electronic appliances. A liquid crystal display consumes less energy and requires less drive force than a cathode ray tube (CRT) so that it allows reduction of size, weight and cost, while it can produce clear and sharp images better than a CRT even in the sunlight. Because of these advantages, the scope of application of liquid crystal display (hereinafter referred to as LCD) has been constantly expanding. Particularly, tremendous efforts have been paid to develop LCDs comprising a film substrate that are thin and lightweight and not damaged even if carried in a pocket of a jacket. As known glass-made LCDs, film-made LCDs are required to have outstanding physical properties. For instance, the components of the cell of the LCD need to be firmly bonded together to provide an enhanced degree of hermeticity. Therefore, they must be physically and chemically stable and resistant against moisture and heat.

Currently, a cell comprising glass substrates and liquid crystal is prepared typically by bonding upper and lower substrates by means of a one-liquid hot-cure type epoxy adhesive, injecting liquid crystal in a highly vacuum condition and sealing the remaining hole by means of a UV (ultraviolet)-light-cure type or two-liquid cold-cure type resin. Improved and highly efficient one-liquid hot-cure type adhesives are currently available and, therefore, there are practically no technological troubles for bonding glass substrates.

On the other hand, one-liquid hot-cure type or two-liquid type epoxy adhesive are used for bonding film substrates. However, a one-liquid hot-cure type epoxy adhesive is originally designed to bond glass substrates and, once cured, it becomes so hard that it is scarcely capable of withstanding bending force and adapting itself to thermal deformations of the bonded substrates and it is rather poorly adhesive to the substrates. A two-liquid type epoxy adhesive is disadvantageous in that it has a relatively short pot life and does not have satisfactory physical and chemical stability to the moisture and the heat of the prepared cell. Sealing materials containing flexible epoxy resin as a principal ingredient such as a polyol type epoxy resin or a urethane type epoxy resin, have been studied, although such materials are not particularly adhesive to film and, to some extent, lack physical and chemical stability to the moisture and the heat of the cells prepared by using such materials. Thus, no satisfactory adhesive has been developed so far for film substrates.

A number of adhesive have been proposed for sealing film-made liquid crystal cells, including one using thermoplastic resin varnish for dissolving the surface of substrates and bonding them by applying heat and pressure thereto (Japanese Patent Application Laid-open No. Shou 57-32669), one using a double bonding technique, where substrates are bonded together by means of a silicone resin type substance on the inside and an epoxy resin type substance on the outside (Japanese Patent Application Laid-open No. Shou 60-69634) and one that cures with heat and light (Japanese Patent Application Laid-open No. Hei 1-129232). None of these, however, has been found commercially feasible.

In view of the above described circumstances, it is therefore an object of the present invention to provide a resin composition for sealing liquid crystal cells that is relatively easy to use, adhesive to film substrates and flexible so that it may be adapted to thermal deformations of the substrates, yet which may be physically and chemically stable to the moisture and the heat of the substrates.

Another object of the present invention is to provide a film-made liquid crystal cell used the resin composition.

As a result of intensive research efforts of the inventors of the present invention, the above object and other objects of the invention are achieved by providing a resin composition comprising epoxy resin that contains a polysulfide modified epoxy resin having a polysulfide structure where a plurality of sulfur atoms are directly linked to chain units in a molecule and an epoxy group is present at each end of the molecule.

A resin composition according to the present invention comprises as principal ingredients epoxy resin containing a polysulfide modified epoxy resin, at least one of hydrazide compounds and at least one of fillers, to which rubber may be added to improve the bond strength and the flexibility of the composition by relieving the stress generated in it when it is cured along with a cure accelerator that reduces the time required for curing at low temperature.

Now, the specific formulations of the resin composition according to the invention will be described below.

Preferably, epoxy resin to be used for the purpose of the invention contains a polysulfide modified epoxy resin expressed by general formula (1)

$$\underset{\diagdown\,O\,\diagup}{CH_2-CH}-R^1-R^2-R^3-\underset{\diagdown\,O\,\diagup}{CH-CH_2} \qquad (1)$$

(where each of R^1 and R^3 represents at least one organic group selected from a group consisting of bisphenol structures, aliphatic oxyether structures and aliphatic thioether structures and R^2 represents a polysulfide structure expressed by $-(C_2H_4OCH_2OC_2H_4S_m)_n-$, wherein m represents the average number of sulfur atoms contained in a polysulfide structure, which is 1 or 2, and n represents the average number of polysulfide structures contained in the above formula, which is between 1 and 50) by 20 to 100% by weight, preferably 50 to 95% by weight, and two or more than two epoxy groups in a molecule, and the average molecular weight of the entire epoxy resin is preferably between 300 and 3,000.

Organic groups selected from a group of bisphenol structures for R^1 and R^3 in formula (1) may include, but not limited to, bisphenol A, bisphenol F, bisphenol AD, bisphenol S as well as alkylated, allylated, acylated and halogenated compounds of them. If the organic groups represented by R^1 and R^3 do not comprise a bisphenol structure, they comprise either an aliphatic oxyether structure or an aliphatic thioether structure.

Additionally, a polysulfide modified epoxy resin to be preferably used for the purpose of the present invention is a disulfide having epoxy groups at the ends and expressed by general formula (2)

$$\underset{\diagdown\,O\,\diagup}{CH_2CH}CH_2S-(C_2H_4OCH_2OC_2H_4SS)_p-C_2H_4O \diagdown \atop \qquad\qquad\qquad \underset{\diagdown\,O\,\diagup}{CH_2CH}CH_2SC_2H_4OCH_2 \qquad (2)$$

wherein p represents the average number of disulfide structures comprised in a molecule, which is between 1 and 15.

Examples of polysulfide modified epoxy resin expressed by general formula (1) above include, if m=2, FLEP-10, FLEP-50, FLEP-60 and FLEP-80 (tradenames: all available from Toray Thiokol Co., Ltd.)

In addition to polysulfide modified epoxy resins, epoxy resins that can be used for the purpose of the present invention include:

(1) polycondensation resins obtained through polycondensation of a compound selected from groups consisting of <1> bisphenols such as bisphenol A and bisphenol F, <2> novolak resin obtained by addition condensation of phenol or cresol and formaldehyde, <3> hydroxy compounds such as tetrahydroxyphenyl methane and resorcinol, <4> amines such as diaminodiphenyl methane, aniline and xylilenediamine, <5> polyhydric alcohols such as glycerol and pentaerythritol, <6> carboxy compounds such as phthalic acid and hexahydrophthalic acid and <7> polyalkylene ether such as ethyleneglycol and its polymers and propyleneglycol and its polymers, and an epihalohydrin such as epichlorohydrin or epibromohydrin and resins obtained through halogenation of such polycondensation resins as well as a polycondensation resins obtained through polycondensation of a compound selected from the groups <1> through <7> above and a methylepihalohydrin such as methylepichlorohydrin and resins obtained through halogenation of such polycondensation resins,

(2) epoxidated aliphatic acids such as epoxidated soy bean oil and its derivatives,

(3) epoxidated diene polymers such as epoxidated polybutadiene and epoxidated polyisoprene,

(4) aliphatic epoxy resins such as 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carbonate and bis(2,3-epoxycyclopentyl)ether and

(5) epoxy resins made flexible through addition of methylene bis(4-phenylisocynate), tolylenediisocyanate, hexamethylenediisocyanate or isoholondiisocynate.

Any of these resins may be used alone or in combination with at least one of the remaining candidate resins.

When the polysulfide modified epoxy resin occupies less than 20% by weight of the total weight of the entire epoxy resin contained in a composition according to the invention, the cured product to be obtained may be too hard or, if not too hard, poorly adhesive to film substrates with markedly reduced physical and chemical stability.

The reason why the average molecular weight of the entire epoxy resin is preferably held between 300 and 3,000 is that, if it is below 300, the cured product to be obtained may be too hard and poorly adhesive to the components of the cell to acquire a desired level of physical and chemical stability.

If, on the other hand, the average molecular weight of the entire epoxy resin exceeds 3,000, it may become poorly resistive to heat and lose any physical and chemical stability. Preferably, the average molecular weight

of the epoxy resin is between 700 and 2,000.

For the purpose of the present invention, at least one of hydrazide compounds may be selected for use from (1) monobasic acid hydrazide compounds such as salicylic acid hydrazide, p-oxybenzoic acid hydrazide, phenylaminopropionic acid hydrazide, lauric acid hydrazide and the like, (2) dibasic acid hydrazide compounds such as succinic acid dihydrazide, adipic acid dihydrazide, isophthalic acid dihydrazide, dodecanoic diacid dihydrazide, carbohydrazide, sebacic acid dihydrazide, thiodipropionic acid dihydrazide, furandicarbonic acid dihydrazide, cyclohexanedicarbonic acid dihydrazide and the like. Of these, dibasic acid hydrazide compounds are particularly suited for the present invention.

Any of these hydrazide compounds works as a curing agent for epoxy resin and, when mixed with epoxy resin, the mixture serves as a one-liquid type epoxy adhesive because it can be stably stored at room temperature. Nevertheless, these hydrazide compounds can start curing a one-liquid type epoxy adhesive at lower temperature and show a better resistivity against heat, cold and moisture than any other curing agents that are conventionally used for a one-liquid type epoxy adhesive such as dicyanodiamide and boron trifluoride. At least one of these hydrazide compounds are preferably used at a ratio of 1/3 to 2/3 mols of hydrazide group to a mol of epoxy group of the epoxy resin contained in the agent. For mixing the two ingredients, a triple-roll mixer may preferably be used for kneading the mixture in order to evenly and finely disperse the hydrazide compound or compounds that are normally solid.

Fillers that can be used for the purpose of the present invention include (1) inorganic fillers including carbonates such as calcium carbonate and magnesium carbonate, sulfates such as barium sulfate, magnesium sulfate, silicates such as aluminum silicate and zirconium silicate, oxides such as iron oxide, titanium oxide, aluminum oxide (alumina), silicon oxide (silica) and zinc oxide, and kaolin, talc, asbestos powder, quartz powder, mica and glass fiber and the like (2) organic fillers such as polyethylene powder, polypropylene powder, polyvinylchloride powder, polystyrene powder, polyvinylacetate powder, polystyrene-polyvinylacetate -copolymer powder, polymethacrylate powder, polyurethane powder, polyester powder, urea resin powder, phenol resin powder, epoxy resin powder and the like. For the purpose of the invention, at least one of these fillers may be selected for use.

While the rate at which at least one of the above listed fillers are added varies depending on the chemical constitution of the resin composition to be prepared and the type of the fillers to be used, typically they are used at a ratio of 1 to 100 portions by weight to 100 portions by weight of the entire epoxy resin. If the fillers are below 1 weight portion, the prepared product might not be smoothly applied and, if applied, the screen-printed patterns might not always be desirable and become inoperative. If, on the other hand, it exceeds 100 weight portions, applying by means of screen-printing can be obstructed. For mixing fillers with a mixture of epoxy resin and at least one of hydrazide compounds, a triple-roll mixer may preferably be used for kneading the mixture and pulverizing the fillers to fine particles in order to avoid clogging a screen at the time of screen-printing operation.

Any rubber that can be graft-copolymerized with epoxy resin of the above identified type so that rubber particles are dispersed in the resin layer formed and can have a so-called sea/islands structure when a resin composition for sealing liquid crystal cells according to the invention is cured may be suitably used for the purpose of the invention.

For the purpose of the present invention, rubber particles may be dispersed into epoxy resin or, alternatively, they may be dissolved into epoxy resin and thereafter deposited when the latter is cured. Still alternatively, rubber particles may be produced in the presence of a graft-copolymer or a copolymer of epoxy resin. Preferably, particles are produced in the presence of a graft-copolymer or a copolymer of epoxy resin because the particle size of rubber particles can be controlled with such a technique. However, any of these techniques can disperse rubber particles in a stable manner as they cause rubber and epoxy resin to interact with each other at the interface. If rubber and epoxy resin do not interact at the interface, the former is apt to agglomerate after having been cured and damage the reliability of the product. If, on the other hand, rubber is appropriately cross-linked, rubber particles are highly resistive against deformation that may be given rise to by the curing stress.

Rubber to be suitably used for the purpose of the invention is preferably of acrylester, silicone, conjugated diene, olefin, polyester or urethane type and more preferably of acrylester, silicone or conjugated diene type. Rubber of any of these types may be used alone or in combination with rubber of any other types.

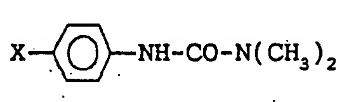
Acrylester type rubber may be used for the purpose of the invention in the form of particles that can be prepared by drying core shell emulsion of the rubber or by means of a method of manufacturing an acrylic acid ester polymer as disclosed in Japanese Patent Application Laid-open No. Shou 55-16053 or a method of manufacturing a graft-copolymer of thermosetting resin and a vinyl polymer as disclosed in Japanese Patent Application Laid-open No. Shou 55-21432, of which the latter method is preferable in terms of dispersion technique and the viscosity after dispersion.

Methods that can be used to prepare silicone type rubber for the purpose of the invention include those utilizing fine particles of silicone rubber (Japanese Patent Applications Laid-open Nos. Shou 60-72957 and Hei 3-170523). According to one of the methods, double bonds are formed in epoxy resin and the epoxy resin is caused to react with silicone containing active hydrogen atoms capable of reacting with double bonds to form a graft-polymer, and then in the presence of the graft-polymer silicone monomers are polymerized. Whereas, with the other method, double bonds are formed in epoxy resin which is caused to react with silicone monomers having vinyl groups that are active for polymerization to produce a graft-polymer, and then in the presence of the graft-polymer silicone rubber monomers are polymerized. However, methods that produce grafted products without utilizing fine silicone rubber particles and prepare rubber particles after the production of grafted products are preferable because such methods can control the size of rubber particles and prevent any undesired rise in the viscosity of the product obtained after dispersing fine particles. Thus, such methods are advantageous for screen-printing a resin composition according to the invention. With these methods, rubber particles and epoxy resin interact with each other at the interface thereof to disperse the former in a well stabilized manner. If, to the contrary, rubber particles and epoxy resin do not interact with each other at the interface thereof, the former is apt to agglomerate after having been cured and to damage the reliability of the product. Additionally, it is desired to be selective in the use of monomers because rubber particles are highly resistive against deformation that may be given rise to by the curing stress if the rubber is appropriately gelled. The above description also holds true for acryl ester type rubber and, therefore, it is preferable to use monomers having glycidyl groups or polyvinyl groups to an appropriate proportion.

Conjugated diene type rubber may be produced through polymerization or copolymerization of monomers of 1,3-butadiene, 1,3-pentadiene, isoprene, 1,3-hexadiene or chloroprene. Rubber articles of this type are also commercially available. A copolymer of butadiene and acrylonitrile which has carboxyl groups or amino groups at the ends of the molecule is particularly advantageous in that it can dissolve in epoxy resin and rubber is deposited at the time of curing so that particles of the produced rubber can be held under control. However, it should be noted that it is difficult to control the particle size of the produced rubber with this technique when compared with the two methods described above (using acryl ester type rubber and silicone type rubber) and the obtained product may be short of satisfactory performance.

For the purpose of the present invention, rubber particles preferably have an average diameter between 0.01 and 5 μm, more preferably between 0.01 and 2 μm and are dispersed throughout the product to show a so-called sea/islands structure. If the average particle size is found out of the above defined range, the obtained product may be short of reliability and satisfactory performance. Rubber is contained in the entire epoxy resin (containing rubber) normally by 0 to 30% by weight and preferably by 2 to 15% by weight. If the rubber content falls below 2% by weight, the final product may not show satisfactory bond strength in a humid atmosphere, whereas if the content exceeds 30% by weight, the prepared resin composition may show an inappropriately high level of viscosity to reduce the efficiency with which the composition is screen-printed and, in some cases, degrade its bond strength after a preliminary drying process. Rubber of any of the above described types may be used alone or in combination with rubber of any other types.

A cure accelerator which may be used for the purpose of the present invention is 3-phenyl-1,1-dimethylurea or 3-p-chlorophenyl-1,1-dimethylurea and expressed by general formula (3) below.



(3)

(where X is a hydrogen or chlorine atom).

For the purpose of the invention, the cure accelerator may be contained in a resin composition according to the invention by 0 to 5% by weight and preferably by 0.2 to 3% by weight. If the content of the cure accelerator falls below 0.2% by weight, the composition may be cured very slowly so that enormous heat and time are consumed. If, on the other hand, the content of the cure accelerator exceeds 5% by weight, it can quickly cure the composition, but it may adversely affect the moisture resistivity and the reactivity with liquid crystal of the composition.

For the purpose of the invention, any known additives may be used with a resin composition according to the invention if they do not adversely affect the effect of the composition. Additives that can be used with a resin composition according to the invention include coupling agents, solvents, thixotropic agents, pigments, dyes, plasticizers, leveling agents, defoaming agents and reactive diluents.

A typical method of manufacturing liquid crystal cells by using a resin composition according to the invention will be described below.

Cell substrates to be used with a resin composition according to the invention are made of a material se-

lected from (1) crystalline thermoplastic resin materials such as polyethyleneterephthalate (PET), polybutyleneterephthalate (PBT), nylon (e.g., 6-6 Ny), polyacetal (POM), polyphenylenesulfide (PPS), polyetheretherketone (PEEK), liquid-crystalline polyester (LCP) and thermoplastic fluorine resin, (2) non-crystalline thermoplastic resin materials such as polycarbonate (PC), modified polyphenyleneoxide (modified PPO), polyarylate (PAR), polysulfone (PSF), polyethersulfone (PES), polyetherimide (PEI) and polyamideimide (PAI) and (3) non-thermoplastic resin materials such as polytetrafluoroethylene (PTFE), polyimide (PI), polyaminobismaleimide and triazine resin. The upper and lower substrates, are normally made of the same kind of resin materials, although they may be made of different resin materials if such materials are feasible for the operation of the produced liquid crystal cell. The surfaces of the substrates may be treated by a surface treating agent such as a silane coupling agent. Additionally, their surfaces to be used for the liquid crystal cell may be attached with the transparent electrodes and the orientation films.

A resin composition comprising epoxy resin containing a polysulfide modified epoxy resin, at least one of hydrazide compounds and at least one of fillers agents, to which a gapping agent (spacer) is added to provide a desired gap, is applied to one of cell substrates to a thickness approximately two to three times greater than the intended thickness of the composition by means of screen-printing, relief printing or a dispenser and precured in a dryer. Thereafter, another substrate to be used for the cell are bonded together and then the aggregate is heated and cured by means of a dryer, a hot plate, a heater block or an infrared heater while applying pressure to the substrates by a collet or a vacuum pin.

A precuring process which may be used for the purpose of the present invention comprises steps of evaporating any solvents and moisture contained in the resin composition and subsequently carrying out a leveling operation so that the resin composition may fit well on the adhesion areas of the substrate to be bonded together. The precuring process is typically conducted in constantly flowing air at temperature between room temperature and 130°C for a period of time between 5 minutes and 6 hours, although it is preferably conducted at temperature between 60 and 110°C for a period of time between 10 and 60 minutes from the viewpoint of cost effectiveness.

A hot-cure (postcure) process to be used for the purpose of the present invention is designed to cause the epoxy resin and the hydrazide compounds of a resin composition to sufficiently react with each other for curing and to bond the cell substrates together by the resin composition. The hot-cure process is typically conducted in constantly flowing air at temperature between 90 and 150°C for a period of time between 5 and 180 minutes and preferably at temperature between 100 and 130°C for a period of time between 30 and 120 minutes.

Examples

Now, the present invention will be described further by referring to a number of examples where resin compositions according to the invention were prepared and liquid crystal cells were prepared by using the resin composition. Note that "portion" and "%" in the following description are those expressed in terms of weight.

The prepared specimens of resin composition for sealing liquid crystal cells and those of liquid crystal panels were evaluated for the following four properties.

(1) operability: This represents an aspect of a resin composition according to the invention required to adapt itself to the entire operation of preparing a liquid crystal panel including screen printing, precuring, bonding and postcuring. The following three ratings were used.

x...poorly operable, Δ...operably but not satisfactorily, o...excellently operable

(2) bond strength: This property of each specimen was determined as follows. Each specimen was applied on a first film substrate (PET, 100mm(width)x100mm(length)x0.1mm (thickness)) by screen printing, precured at 90°C for 20 minutes and then cooled to ambient temperature. A second film substrate (PET, 0.1mm thick) was bonded thereto and the two substrates were pressed against each other by a press jig and postcured at 120°C for 90 minutes. The combined substrates were then cut to produce ten 10mm wide test pieces (100mm(length)x10mm(width)). The screen printing was conducted in such a way that the specimen was applied to each test pieces to occupy an area of 1mmx50mm with a thickness of 5 μm at the center. Immediately after preparing the test pieces and after they were immersed in boiled water for 3 to 5 hours, they are tested for T-peel test according to JIS-K-6854.

(3) flexibility: Each of the above pieces was bent and loaded with a 1kg weight for 10 seconds to see if any breaking was observed at the bent section. If not, the pieces was bent to the reverse side and subjected to a second load test. The above procedures were repeated whenever necessary. The following five ratings were used.

x...broken at the first test, x~Δ...broken at the second test, Δ...broken at the third test, Δ~o...broken at the fourth test, o...not broken before the fifth test

(4) electric property: Immediately after preparing liquid crystal panels and after they were exposed to an

atmosphere of 80°C and 95%RH for 500 hours, an electric current was made to run between the terminals of each specimen to see its rate of change (coefficient).

Synthesis Example 1

A following rubber substance was synthetically prepared as an ingredient of a specimen.

A 12 portions of acrylic acid and a 1 portion of triethylamine were added to a 600 portions of bisphenol F type epoxy resin prepared from bisphenol F and epichlorohydrin (EPICLON 830S: tradename, available from DAINIPPON INK AND CHEMICALS, INC.), which were then caused to react mutually by heating to 110°C for 5 hours to produce a 613 portions of epoxy resin containing acrylic group. Subsequently, a 350 portions of butylacrylate, a 20 portions of glycizdylmethacrylate, a 1 portion of divinylbenzene, a 1 portion of azobisdimethylvaleronitrile and a 2 portions of azobisisobutylonitrile are added to the above product and a polymerization process was carried out on the mixture at 70°C for 3 hours and then at 90°C for an hour to produce a graft-polymer of epoxy resin and acrylester. Fine particles of the polymer (A-1) had an average particle size of 0.05 μm and presented a so-called sea/islands structure. The epoxy equivalent and the rubber content of the polymer were respectively 305g/eq and 37.9%.

Synthesis Example 2

A 613 portions of epoxy resin containing acrylic group were prepared, following the former half procedures of Synthesis Example 1. Subsequently, a 5 portions of hydroxyethylacrylate, a 10 portions of butylacrylate and a 2 portions of azobisisobutylonitrile were added to the above epoxy resin and a polymerization process was carried out on the mixture at 70°C for 3 hours and then at 90°C for an hour to produce a graft-polymer of epoxy resin and acrylester. Then, a 70 portions of a silicone intermediate having a methoxy group in each molecule and a 300 portions of a 1:1 mixture solution of a two-liquid cold-cure type silicone rubber were added to the graft-polymer and the mixture was stirred for 3 hours for reaction to produce a silicone modified epoxy resin. Fine particles of the obtained polymer (A-2) had an average particle size of 3.5μm and presented a so-called sea/islands structure. The epoxy equivalent and the rubber content of the polymer were respectively 281g/eq and 33.0%.

Examples 1 through 9

The ingredients as listed in Table 1 were mixed in a Henschel or Dalton mixer or a ball mill and then kneaded in a ceramic triple-roll mixer for each example until the particles of the fillers and curing agents became smaller than 10μm in diameter. Then, a 100 portions of the kneaded material and a 3 portions of a spacer agent (milled fiber with a particle diameter of 5μm) were mixed well at room temperature to obtain a specimen of resin composition for sealing liquid crystal cells. Each specimen was applied on a first film substrate (PET, 0.1mm (thickness)) by screen printing, precured at 90°C for 20 minutes and then cooled to ambient temperature. A second film substrate (PET, 0.1mm thick) was bonded thereto and the two substrates were pressed against each other by a press jig and postcured at 120°C for 90 minutes to produce a blank panel (liquid crystal cell). Then, biphenyl type liquid crystal was poured into the blank panel through a sealing hole, which was subsequently sealed with STRUCT BOND ES-302 (tradename: two-liquid cold-cure type epoxy resin available from MITSUI TOATSU CHEMICALS, INC.) to produce a finished film-made crystal panel.

The obtained specimens of resin composition for sealing liquid crystal cells and the liquid crystal panels were evaluated by the above described tests. Table 3 shows the results of the tests on these specimens and panels.

Comparative Examples 1 through 8

Comparative specimens of resin composition for sealing liquid crystal cells and liquid crystal panels were prepared by using ingredients as listed in Table 2 and the process as described above for Examples 1 through 9. The obtained specimens and panels were evaluated by the above described tests. Table 3 also shows the results of the tests.

Table 1

unit: portion

	Examples 1	2	3	4	5	6	7	8	9
epoxy resin									
epoxy resin A (*1)					80	40			
epoxy resin B (*2)						40			
epoxy resin C (*3)									
epoxy resin D (*4)									
polysulfide modified epoxy resin									
A (*5)	100			50			35	45	100
B (*6)		100				20			
C (*7)			100	50	20		35	45	
rubber A-1								10	
A-2							30		
average molecular weight	720	660	1000	860	500	920	2100	1070	720
curing agent									
DDH (*8)	14	16	10	12	24	16	14	13	14
PAA (*9)									
polythiol (*10)									
cure accelerator									
A (*11)	2	2	2	2	2	2	2	2	
B (*12)									2
filler									
alumina	10	10	10	10	10	10	10	10	10
thixotropic agent									
AEROSIL (*13)	5	5	5	5	5	5	5	5	5

Table 2

unit: portion

	Comparative Examples							
	1	2	3	4	5	6	7	8
epoxy resin								
epoxy resin A (*1)	85						85	85
epoxy resin B (*2)								
epoxy resin C (*3)		85						
epoxy resin D (*4)			85	100	70	55		
polysulfide modified epoxy resin								
A (*5)		26						
B (*6)								
C (*7)	15		15			15	15	15
rubber A-1					30	30		
A-2								
average molecular weight	470	660	580	500	1250	1330	470	470
curing agent								
DDH (*8)	25	16	25	17	17	16		
PAA (*9)							117	
polythiol (*10)								214
cure accelerator								
A (*11)	2	2	2	2	2	2		
B (*12)								
filler								
alumina	10	10	10	10	10	10	10	10
thixotropic agent								
AEROSIL (*13)	5	5	5	5	5	5	5	5

*1: bisphenol F/epichlorohydrin polycondensation type epoxy resin
tradename: EPICLON 830S, available from DAINIPPON INK AND CHEMICALS, INC.
average molecular weight 380
epoxy equivalent 185~195g/eq

*2: bisphenol A/epichlorohydrin polycondensation type epoxy resin
tradename: Epikote 1004, available from Yuka Shell Epoxy Co., Ltd.
average molecular weight 1,600
epoxy equivalent 875~975g/eq

*3: chain epoxy resin
tradename: Adeka Resin EP-4000, available from ASASHI DENKA KOGYO K.K.
average molecular weight 650
epoxy equivalent 310~340g/eq

*4: urethane modified epoxy resin
tradename: Adeka Resin EPU-11, available from ASAHI DENKA KOGYO K.K.
average molecular weight 500
epoxy equivalent 285~335g/eq

*5: polysulfide modified epoxy resin, FLEP-10
available from Toray Thiokol Co., Ltd.
average molecular weight 720
epoxy equivalent 330~390g/eq

*6: polysulfide modified epoxy resin, FLEP-50
available from Toray Thiokol Co., Ltd.
average molecular weight 660
epoxy equivalent 300~360g/eq

*7: polysulfide modified epoxy resin, FLEP-80
available from Toray Thiokol Co., Ltd.
average molecular weight 1,000
epoxy equivalent 450~550g/eq

*8: dodecanoic diacid dihydrazide

*9: polyamideamine
tradename: Versamid 125
available from Henkel Hakusui Corp.
amine value 330~360mg-KOH/g

*10: polythiol (mercaptan)
tradename: ATO CX-1, ATCHEM JAPAN
SH value 6.70 mg-KOH/g

*11: 3-p-chlorophenyl-1,1-dimethylurea
available from Tokyo Kasei Kogyo Co., Ltd.

*12: 3-phenyl-1,1-dimethylurea
available from ACI Japan Ltd.

*13: AEROSIL #200 (tradename), available from Nippon Aerosil Co., Ltd.

Table 3

	operability	bond strength (kg/10mm)			flexibility	electric property (coefficient)
		0hrs	3hrs	5hrs		
Example 1	o	2.4	2.4	2.2	o	1.72
2	o	2.2	2.1	1.6	o	1.82
3	o	2.3	2.0	1.5	o	1.91
4	o	2.9	2.7	2.7	o	1.78
5	Δ	1.4	1.3	1.2	Δ~o	2.23
6	Δ	1.2	1.3	1.1	Δ~o	2.19
7	o	3.7	3.4	3.1	o	1.58
8	o	3.1	3.0	2.6	o	1.64
9	o	2.5	2.3	2.2	o	1.83
Comparative Example 1	o	0.8	0.5	0	x~Δ	-
2	o	0.7	0.6	0.2	x	-
3	o	0.4	0.2	0	x	-
4	Δ	0.1	0	0	x	-
5	o	0.5	0.3	0.3	x	5.89
6	o	0.3	1.2	1.0	x~Δ	3.65
7	x	0.3	0	0	x	-
8	x	0.4	0	0	x	-

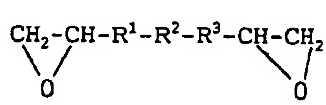
B.N.: "-" denotes a test impossible status due to breaking after keeping for 500 hours in atmosphere of 80°C and 95%RH.

Claims

1. A resin composition for sealing liquid crystal cells comprising as principal ingredients (1) epoxy resin containing a polysulfide modified epoxy resin, (2) hydrazide compounds and (3) fillers.

2. A resin composition according to claim 1, wherein the entire epoxy resin contains said polysulfide modified epoxy resin by 20 to 100% by weight.

3. A resin composition according to claim 1 or claim 2, wherein said polysulfide modified epoxy resin is expressed by general formula (1)



(1)

wherein each of R^1 and R^3 represents at least one organic group selected from a group consisting of bisphenol structures, aliphatic oxyether structures and aliphatic thioether structures and R^2 represents a polysulfide structure expressed by $-(C_2H_4OCH_2OC_2H_4S_m)_n-$, where m represents the number of sulfur atoms contained in a polysulfide structure, which is 1 or 2, and n represents the average number of polysulfide structures contained in the above formula, which is between 1 and 50.

4. A resin composition according to any one of the preceding claims, wherein the average molecular weight of the entire epoxy resin is between 300 and 3,000.

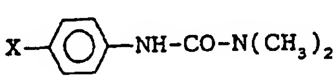
5. A resin composition according to any preceding claim wherein the epoxy resin contains rubber which is a graft-copolymer of epoxy resin.

6. A resin composition according to claim 5, wherein fine particles of rubber of an acrylester type, a silicone type, a conjugated diene type or a mixture thereof having a particle diameter of 0.01 to 5μm are dispersed in the epoxy resin.

7. A resin composition according to claim 5 or claim 6, wherein the epoxy resin contains rubber by 2 to 30% by weight.

8. A resin composition according to any preceding claim further containing a cure accelerator that is a urea compound.

9. A resin composition according to claim 8, wherein the cure accelerator is expressed by general formula (3)



(3)

(where X is a hydrogen or chlorine atom).

10. A resin composition according to claim 9 containing 0.2 to 5% by weight of the urea compound.

11. A film-made liquid crystal cell prepared by applying a resin composition according to any one of the preceding claims to film-made cell substrates, precuring the resin composition and thereafter hot-curing it to bond the substrate.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 4686

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	DATABASE WPI Derwent Publications Ltd., London, GB; AN 84-216318 & JP-A-59 126 511 (MITSUI TOATSU) 21 July 1984 * abstract *	1-10	C08G59/40 C08G59/30 G02F1/1339
Y	PATENT ABSTRACTS OF JAPAN vol. 13, no. 115 (C-578) 20 March 1989 & JP-A-63 289 015 (TORAY) 25 November 1988 * abstract *	1-10	
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 93-191679 & JP-A-5 117 532 (TOSHIBA) 14 May 1993 * abstract *	1	
A	US-A-5 150 239 (Y. WATANABE, E.A.) * column 3, line 30 - column 4, line 42; claims * * column 5, line 19 - line 40 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 82-82861E & JP-A-57 137 317 (MITSUI TOATSU) 24 August 1982 * abstract *	1	C08G G02F
A	EP-A-0 013 875 (SIEMENS) * page 4, line 1 - line 16; claims *	1	
A	US-A-3 856 933 (E. M. JANKOWIAK, E.A.) * column 2, line 62 - column 3, line 49; claims; examples *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	2 November 1994	Deraedt, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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